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Photoswitchable Sexithiophene-Based Molecular Wires

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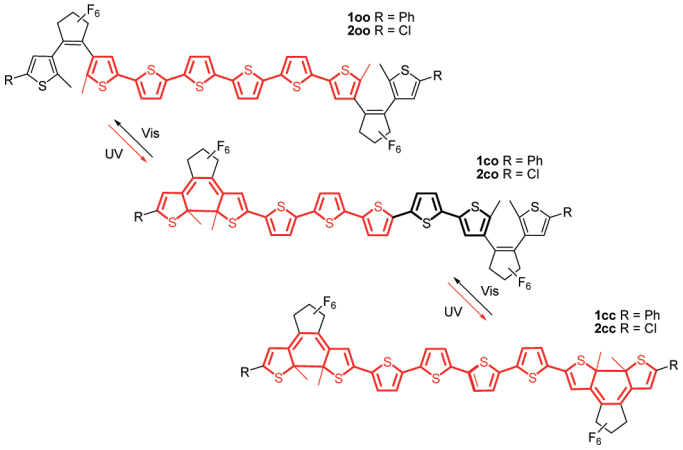
ABSTRACT



Photochromic sexithiophenes were prepared by oxidative electrochemical coupling of terthiophenes. The redox properties in the open state are typical of sexithiophenes. Ring closure of both photochromic units leads to a decrease in the energy of the LUMO orbitals with little affect on the energy of the HOMO orbitals. The photochemical tuning of the conjugation of a molecular wire is achieved by combining dithienylethene units with a sexithiophene.

The electronic properties of polythiophenes are remarkable in comparison to semiconductor and metallic nonmolecular materials, especially considering the range of conductivities that can be accessed through synthetic tuning and processing.[1] Furthermore, their stability toward dioxygen and water has facilitated their application in organic electronic devices.[2] Understanding the electronic and photonic properties of polythiophene materials is key to the molecular design of components for application in electronic devices.[3] In this regard, oligothiophenes offer considerable advantages over polythiophenes due to the precisely defined structures that can be prepared and probed electrochemically and spectroscopically.[4] α,α′,α″-Sexithiophene and its derivatives[5] have

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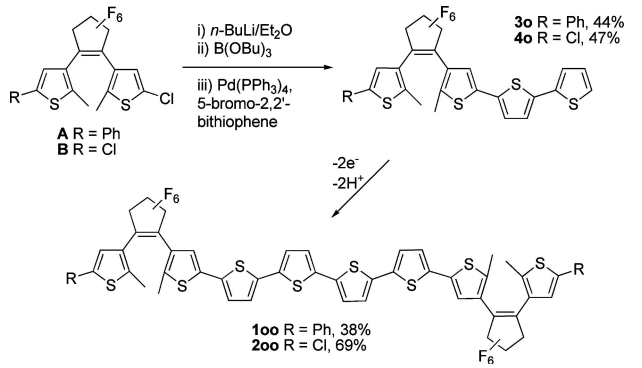
attracted widespread interest in recent years not only as models for polythiophenes but also in their own right as versatile active components in electronic devices such as electrochromic materials,[6] field-effect transistors,[7] OLEDs,[8] molecular wires,[9] and photovoltaic cells.[10] Control over their electronic properties can be achieved through synthetic modification[11] or postsynthetically through processing. Postsynthetic tuning of properties by external stimuli, specifically light through incorporation of a photoresponsive unit, is an attractive alternative, but is considerably more challenging due to the ability of oligothiophenes to quench excited states efficiently.[12] Tsivgoulis and Lehn demonstrated that when substituted with ter- and tetrathiophene units the photochromism of the dithienylethene unit is retained and enables photoswitching of conjugation pathlengths.[13]

Recently, we demonstrated[14] related systems, in which photochromic units, i.e., dithienylcyclopentenes, that could be used as switching elements to control the electropolymerizability of α,α′-alkene-bridged bis-terthiophene monomers. In the ring-open state, electropolymerization to form alkene-bridged sexithiophene polymers proceeded smoothly. However, ring closure of the dithienylethene unit[15] of the monomer with UV light resulted in a complete inhibition of polymer formation. Subsequent ring opening with visible light restored the electropolymerizability of the monomer. The dithienylethene/sexithiophene polymer films obtained, however, were photochemically inert both in terms of photoluminescence and photochromism. The key fundamental question facing the development of switchable sexithiophene systems is: Can we combine multiple dithienylethenes units with sexithiophene and retain the photochromic properties of dithienylethenes?

Here, we report the synthesis and spectroscopic and electrochemical characterization of two sexithiophene-based compounds **1** and **2** (Scheme 1), which incorporate photo-

Scheme 1. Synthesis of **1oo** and **2oo**



switchable dithienylhexafluorocyclopentene units, to address this question. Compounds **1** and **2** can be viewed as either a dimer of photochromic dithienylethenes bridged by a tetrathiophene unit or alkene/methyl end-capped sexithiophenes. We demonstrate that dithienylethene photochromic units can retain their photochromic functionality when part of an extended π-conjugated sexithiophene system. Furthermore, the effect of a change in a, essentially peripheral, substituent (i.e., phenyl- vs chloro-), on the properties of these systems is found to be stronger than would be anticipated. The present systems are complementary to those of Tsivgoulis and Lehn[13] (vide supra) in that here the sexithiophene unit is retained in all three photochromic states.

The approach taken here to prepare the photochromic sexithiophene systems is based on the electrochemically driven coupling of two terthiophene units via their radical cation oxidation states. α-Dimerization[1c,5b,16] offers advantages as a complementary route to preparing sexithiophenes, in particular to the metal-catalyzed (Sn, Pd, etc.)[17] coupling reactions or chemically induced oxidative coupling with ferric chloride.[18] The terthiophene-based diarylethene photochromic switches **3o** and **4o** were obtained using methods reported earlier for the preparation of asymmetric dithienylethenes (Scheme 1).[19] Cyclic voltammetry indicated that as for the electropolymerizable system reported earlier,[14] oxidation did not lead to ring closure but instead to dimerization.

The preparation of **1oo** and **2oo** through α-dimerization of **3o** and **4o**, respectively, was carried out by potentiostatic

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(19) See the Supporting Information.

oxidative coupling at ca. 1.10 V (vs SCE, 1 mM in 0.1 M KPF_6/CH_3CN). The light yellow solutions turned dark green upon oxidative electrolysis and subsequently deep yellow upon standing or after the applied potential was switched to 0.1 V vs SCE. **1oo** and **2oo** were purified by preparative thin-layer chromatography and characterized by ^1H and ^{13}C NMR spectroscopy and by MALDI-TOF mass spectrometry.[19]

X-ray structural analysis (Figure 1)[19] reveals that **1oo** is located at a crystallographic inversion center and the

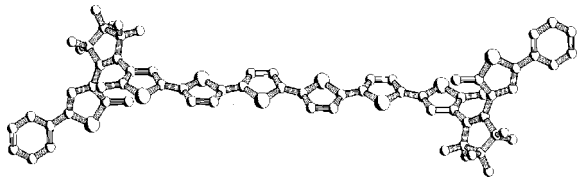

Figure 1. Molecular structure of **1oo**.

sexithiophene moiety is essentially planar. It exhibits an all-anti, anti conformation that reduces steric interaction between the thiophene units; however, the high conversion to **1cc** in solution (vide infra) confirms that the syn and anti conformations are in dynamic equilibrium in solution.

Comparison of the FTIR spectra of **1oo/2oo** with **3o/4o**, respectively,[19] shows that the characteristic absorptions (i.e., C−F stretching) of the hexafluorocyclopentene units are retained.[20] Notably for both **3o** and **4o** the characteristic C−H oop bending of the terminal thiophene C−H, at 690 cm^{-1},[21] is absent in the α,α′-dimerization products **1oo** and **2oo**. The absorption band at 790 cm^{-1} in the spectra of **1oo** and **2oo** is characteristic of a sexithiophene.[22]

The influence of the sexithiophene unit on the physical properties of the dithienylethene units, and vice versa, was examined spectroscopically and electrochemically. The UV−vis absorption, fluorescence, and electrochemical data for **1**−**4** (see the Supporting Information) are summarized in Table 1. The absorption and emission spectra and the cyclic voltammetry of **1oo** and **2oo** (Figure 2) are characteristic[23] of end-capped sexithiophenes. For both **1oo** and **2oo**, two sequential reversible ($E_{p,a} - E_{p,c} \sim 60-80$ mV) redox processes (e.g., **1oo** → **1oo**$^+$ and **1oo**$^+$ → **1oo**$^{2+}$) are observed. The absorption spectrum of **1oo** is red-shifted significantly compared with that of **2oo** by ∼2700 cm^{-1}. The shift of the first and second oxidation waves by 190 mV indicates that the chloro/phenyl-substituted thiophene end groups affect both the HOMO and LUMO levels, albeit with significantly more stabilization of the HOMO. Furthermore, the effect of the substituents on the fluorescence of **1oo** and **2oo** is significant with a 3-fold decrease in the fluorescence quantum yield. A more pronounced vibronic progression is observed for **1oo** than for **2oo**. Notably, in contrast to their absorption spectra, the energies of the emission maxima of **1oo** and **2oo** are similar. Considering the relative remoteness of the phenyl/chloro substituents from the sexithiophene unit, the data indicate that the alkene bridge mediates electronic intercomponent communication effectively.

Table 1. Electronic Absorption, Fluorescence, and Redox Data

	abs λ_{max}/nm ($\varepsilon/10^3$ $M^{-1}cm^{-1}$)	em $\lambda_{max/nm\ (\Phi)}$[d]	$E_{p,c}$/V	$E_{1/2}$/V (vs SCE)
1oo	270 (40.2), 435 (41.0) 307 (23.0), 392 (18.0),	504 (0.28)[c]	−1.80	0.83, 1.04
1cc	468 (20.0), 634 (44.0) 246 (52.0), 357 (40.0),		−1.47, −1.14, −0.96	0.79, 0.85
2oo	389 (sh)	499 (0.09)[b]		1.02, 1.22
2cc	374 (37.0), 567 (36.0)			
3o	260 (32.6), 354 (31.0)	413[a]		1.13 (irr)[e]
3c	282 (21.7), 385 (26.0), 401 (27.0), 604 (24.0)			0.78, 0.95
4o	250 (18.2), 355 (18.1)	407[a]		1.34 (irr)[e]
4c	384 (16.0), 565 (13.5)			0.92

[a] λ_{ex} = 350 nm. [b] λ_{ex} = 367 nm. [c] λ_{ex} = 430 nm. [d] Measured against 9,10-diphenylanthracene (Φ_{fl} = 0.90 in cyclohexane).[24] [e] irr = a return cathodic wave is not observed ($E_{p,a}$ only), sh = shoulder.

Importantly, bulk oxidation of the open form (e.g., **1oo**$^{2+}$) does not lead to formation[25] of the ring-closed state (e.g., **1cc**$^{2+}$). Reduction of **1oo**$^{2+}$ and **2oo**$^{2+}$ leads to a full recovery of the spectrum of the neutral forms **1oo** and **2oo**, respectively. The absence of a significant influence of the phenyl and chloro substituents on the absorption spectra of the monocations and the absence of electrochemical ring closure suggest that the polaron is localized on the sexithiophene core. This model is supported by DFT calculations on **1oo** which show that the frontier molecular orbitals are localized on the sexithiophene.[19] Irradiation of the **1oo**−**4o** with UV light results in the appearance of a new absorption band that is characteristic of photochemical ring closure of the dithienylperfluorocyclopentene unit.[15d] The photochromic response is reversed upon irradiation with visible (>500 nm) light. For all compounds, the intensity of the fluorescence decreases by >98%, indicating that at the photostationary state at 365 nm (PSS) essentially complete conversion of **1oo** to **1co/1cc** is achieved.

For the terthiophene-substituted diarylethenes **3o** and **4o**, irradiation with UV light results in the formation of the ring-closed forms **3c** and **4c**, respectively. For **1oo** and **2oo** there is the possibility of forming two photoproducts, i.e., where one or both of the dithienylethene units are in the closed state. HPLC analysis indicates that the ring closure proceeds via the closed/open state to the closed/closed state (e.g., **1cc**, see graphical abstract). Isolation of **1co** and **1cc** was precluded by the thermal instability of both states toward ring opening to **1oo**.[19] Comparison of the UV/vis spectra of

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each compound obtained by HPLC[19] with the spectra obtained at the PSS indicates that the PSS consists of >90% of **1cc**.

As for the open state, the lowest energy absorption band of the phenyl-substituted **1cc** is red-shifted by ca. 1800 cm^{-1} with respect to the chloro-substituted **2cc**. The effect of the substituent on the absorption spectrum in this case, however, is not unexpected considering the contribution of the bis-*trans*-butadiene unit of the closed dithienylcyclopentene to the (HOMO/LUMO) frontier orbitals. The redox chemistry of **1oo** and **1cc** is shown in Figure 2c. The effect of ring closure on the first oxidation potential is minimal with the separation between the first and second oxidation process decreasing upon ring closure. By contrast, the change in the reduction potential is typical of dithienylethenes with a positive shift in the first reduction potential of 840 mV (6700 cm^{-1}) which corresponds closely to the shift in the lowest energy absorption band upon ring closing (ca. 7200 cm^{-1}).[25] The frontier molecular orbital diagrams obtained from DFT calculations[19] suggested that upon closing of the dithienylethene rings the system can best be described as two closed dithienylethenes rather than an end-capped sexithiophene. That is, the properties are not those of a sexithiophene but instead are those of a dithienylethene. This provides a rationalization for the decrease in the separation of the first and second oxidation steps upon ring closing. For a hexafluorocyclopentene bridged dithienylethene the separation between the first and second oxidation is typically less than 80 mV. Furthermore the ring opening to form $\mathbf{1oo}^{2+}$ that follows oxidation of **1cc** to $\mathbf{1cc}^{2+}$ explains why electrochemically driven ring closing is not observed in either **1oo** or **2oo**.[19]

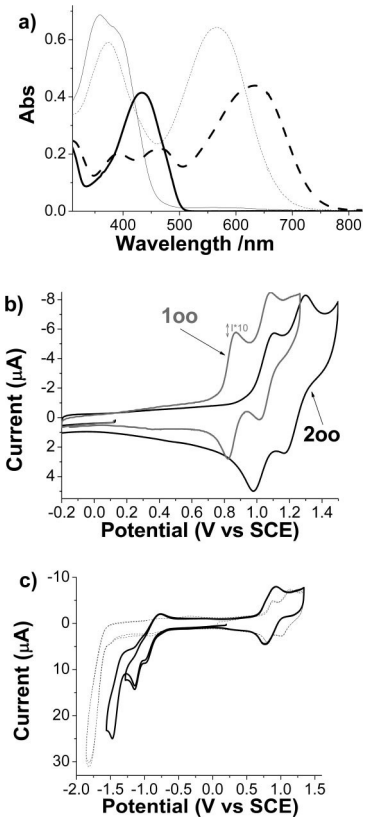

Figure 2. (a) UV−vis absorption spectra of **1oo** (thick solid), **1cc** (thick dashed), **2oo** (light solid), and **2cc** (light dashed) in hexane. **1cc** and **2cc** were obtained by irradiation of **1oo** and **2oo**, respectively, at λ_{exc} 365 nm.[20] Cyclic voltammetry of (b) **1oo**, 0.01 V s^{-1} and **2oo**, 0.1 V s^{-1} and (c) of **1oo** (dotted) and **1cc** (PSS 365 nm solid) 0.1 V s^{-1} in CH_2Cl_2/0.1 M $TBAPF_6$.

In summary, we have shown that end-capped sexithiophenes, which incorporate the functionality of dithienylethene photochromic switches, can be prepared conveniently by electrochemical dimerization. These hybrid systems can be switched between three electronic states, i.e., **1oo**, **1co**, and **1cc**. The photochemical activity of these end-substituted sexithiophenes demonstrates that the photochromism of the dithienylcyclopentene motif is retained when part of a sexithiophene "molecular wire". This indicates that the absence of photochemistry in films of a related dithienylethene/sexithiophene-based polymer is due to intermolecular excited-state quenching and not intramolecular quenching of the photochemistry of the dithienylethene units by the sexithiophene unit.

Finally, it is clear that the hexafluorocyclopentene unit provides for a remarkable degree of communication between the peripheral and core units. The ability of a simple electron-deficient alkene bridge to allow for relatively remote substituents to be used to tune the properties of the sexithiophene core opens up new possibilities in the molecular tuning of this important material for organic electronics. Detailed photophysical studies of these systems will be reported in due course.

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Supporting Information Available: Synthetic procedures and NMR, IR, UV/vis-NIR spectroscopic and electrochemical characterization, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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